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The Effects of Heat Treatment Atmosphere on the Bone-Like Apatite Inducement on the Alkali Treated Ti-6Al-4V Surfaces

Chi-Fen Lu[a], Hsin-Ming Huang[a], Chun-Hui Chu[a], Wang-Long Li[b], Ting-Fu Hong[a,]*

[a]*Department of Materials Engineering, National Pingtung University of Science and Technology, Pingtung, Taiwan, ROC.*
[b]*Department of Materials Science and Engineering, National Cheng-Kung University, Tainan, Taiwan, ROC.*

Abstract

The purpose of this study is to investigate the bone-like apatite inducement ability on the 5M NaOH, deionized water and 600°C atmospheric or vacuum heat treated Ti-6Al-4V surfaces in the modified simulated body fluid (m-SBF) solutions. The alkali-heat treated specimens were soaked in m-SBF up to 7 days for their bioactivity evaluation and induced bone-like apatite layer investigation. All the samples were characterized their surface morphology, chemical and bioactivity by SEM, EDX, XRD and contact angle analysis, respectively. The experimental results show that a thin HA-rich bone-like apatite layer was formed along all the alkali-heat treated Ti-6Al-4V surfaces within 5 days after soaking in the m-SBF. It is also found the alkali-atmospheric heat treated Ti-6Al-4V samples have more favourable bioactivity than alkali-vacuum heat treated counterparts.

Keywords: Alkali treatment; heat treatment; simulated body fluid; bone-like apatite; Ti-6Al-4V

* Corresponding author. Tel.: +886-8-7703202; fax: +886-8-7740552 .
E-mail address: tfhong@mail.npust.edu.tw .

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1. Introduction

Titanium (Ti) and its alloys are ideally suitable for medical implants due to their favourable mechanical and biological compatibilities. However, such metals are bioinert, and therefore do not easily form chemical bonds with the host tissue. Thus, to create a bioactive layer on their surfaces for direct bonding capability to the surrounding tissues is normally considered for a permanent implant applications [1-2].

Various methods are applied to coat a thin layer of bioactive material such as hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) on the metal implant surfaces, such that chemical bonds are formed between the implant and the surrounding bone tissue following implantation [3-4]. The HA coating on the implant is predominantly fabricated using sol–gel coating [5-8], electrochemical deposition [9-10], or plasma spraying methods [11-12]. Plasma spraying technique has been widely used on such purpose nowadays. However, there are still some insufficient problems arising during this process. For example, the high temperature (over 6000°C) generated during the process may degrade the crystallinity and phase composition of HA, and therefore reduces the adhesive and biological performances [13-15].

Recently, there has been an increasing interest in utilizing simple chemical and biomineralisation methods to treat and bioactivate Ti and its alloys surfaces at a relatively low temperature, especially for samples with a complex shape or porous structure [16]. The concept of sol-gel and following biomimetic mineralization was inspired by Kokubo and his colleagues from 1990 [17-22]. A layer of calcium phosphate is produced on those surfaces with active chemical groups, which serve as nucleation sites for mineralization [21].

The purpose of this study is to investigate the bone-like apatite inducement ability on the 5M NaOH, deionized water (DI water) and 600°C atmospheric and the vacuum heat treated Ti-6Al-4V surfaces. All the samples were soaked in m-SBF [21] for up to 7 days for the formation of bone-like apatite layer and then characterized their surface morphology, chemical and wet abilities by SEM, EDX, XRD and contact angle analysis, respectively.

2. Experimental

2.1. Sample preparation

Ti-6Al-4V substrates were sliced into thin plates with dimension of 10mm×10mm×1mm. The plates were ground using 120, 240, 400 and 600 grit SiC paper in order. All substrates were ultrasonically cleaned in acetone, ethanol and pure water to remove possible impurities introduced during sectioning and grinding. The sliced samples were immersed in a 5M NaOH aqueous solution and then DI water at 60°C for 24 hours each. Samples were then heat-treated at 600°C for 1 hour under atmosphere (1 atm) or vacuum (0.921 atm) condition, respectively.

2.2. Bioactivity evaluation

The alkali-heat-treated samples were soaked in an m-SBF at 36.5°C up to 7 days for bioactivity evaluation. The m-SBF were prepared by dissolving reagent-grade chemicals of sodium chloride (NaCl), sodium hydrogen carbonate ($NaHCO_3$), sodium carbonate (Na_2CO_3), potassium chloride (KCl), dipotassium hydrogen phosphate trihydrate ($K_2HPO_4 \cdot 3H_2O$), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), calcium chloride ($CaCl_2$), and sodium sulphate (Na_2SO_4) into deionised water. 1.0 M NaOH was used to buffer the solution to pH 7.40 at 36.5°C.

2.3. Characterization of surface properties

The surface morphology of the samples was examined by scanning electron microscopy (SEM, HITACHI S-3000N). The elements and phases that contained in surface structures were analyzed by energy dispersive X-ray spectroscopy (EDX) equipped in SEM, and X-ray diffractometry (XRD, BRUKER D8 ADVANCE), respectively. The XRD was performed at 2θ angles from 20º to 60º at a scanning speed of 0.6º/min. The wettability of the surfaces was evaluated by contact angle measurement (First Ten Angstroms 1000), where m-SBF was used as the test medium. All the samples were coded and summarized in Table 1 for convenient purpose.

Table 1. An example of a table.

Code	Sample
Ti-6Al-4V	As cleaned Ti-6Al-4V
5M	Ti-6Al-4V after alkali treatment
5M-W	Ti-6Al-4V after alkali and DI water treatments
5M-W-H	Ti-6Al-4V after alkali, DI water and atmospheric heat treatments
5M-W-V	Ti-6Al-4V after alkali, DI water and vacuum heat treatments

3. Results and Discussion

3.1. Surface morphological and chemical characterizations after alkali-heat treatments

Figure 1 schematically illustrates the cross-sectional view of samples showing three zones: coating layer, interfacial layer and substrates. Scanning electron microscopy was conducted to characterise the surface morphology evolution of Ti samples after each treatment. Figure 2 shows the surface SEM images of alkali, alkali-DI water and alkali-DI water-heat treatments samples, respectively. It is noted that the submicron-sized porous network structure was formed after the alkali treatment. The thickness of coating layers was increased with the steps of treatments, and the 5M-W-H has the relatively thicker one. It is also found that the surfaces of 5M-W-H sample contain a relatively higher amount of oxygen then other ones by EDX.

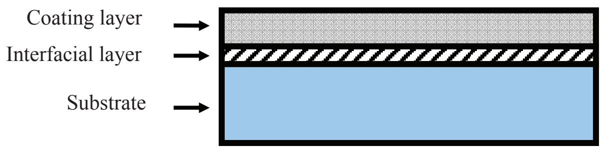

Fig. 1. Schematic illustration of sample's cross section.

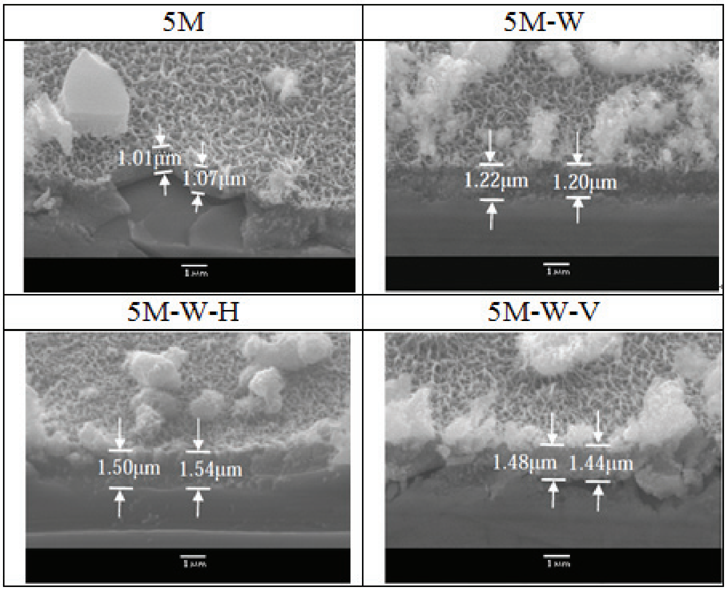

Fig. 2. Surface morphology of samples after alkali, DI water, atmospheric/vacuum treatments, respectively.

The wettability was used for estimating the bioactivity of the specimen. Figure 3 reveals that the contact angle of the samples has an apparently decrease after alkali treatment. The 5M-W-H has the lowest value among entire specimens, which is expected that has the best bone-like apatite inducement ability.

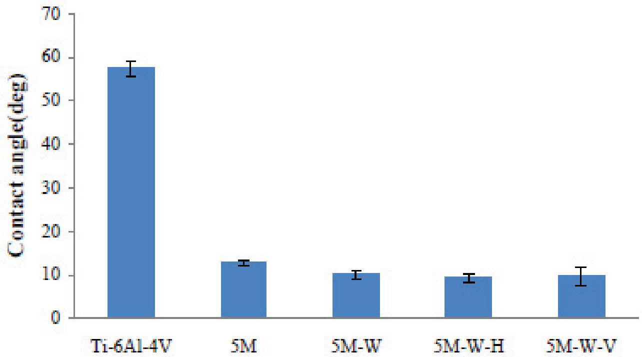

Fig. 3. The contact angle measurement of samples after cleaning, alkali, DI-water, and heat treated at different atmosphere conditions, respectively.

3.2. Evaluation of bone-like apatite inducement in m-SBF

The alkali-DI water-heat treated samples were soaked in the prepared m-SBF at 36.5ºC in an incubator for up to 7 days to evaluate their apatite forming ability (bioactivity). Overall, from the SEM images in

Fig. 2, it can be seen clearly that the porous structures were uniformly covered on the Ti-6Al-4V surfaces before the bioactivity examination. Figure 4 reveals that some P/Ca-rich structures started to form on the porous structure after soaking in m-SBF for 3 days and a layer of coating was formed on the surfaces after immersion for 5 days and those thereafter. Both atmospheric and vacuum heat treated samples showed successful bioactivity.

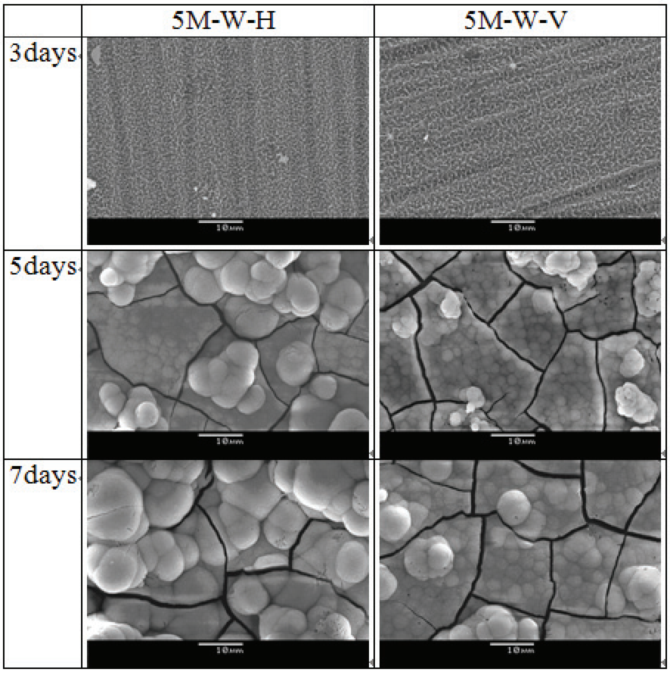

Fig. 4. SEM images of sample surfaces after soaking in m-SBF for various days.

XRD was utilized for characterizing the structures formed on the surfaces each process. Figures 5 and 6 reveal the XRD profile evolution of the alkali-DI water-atmospheric heat treated set samples and alkali-DI water-vacuum heat treated counterparts after each treatment. Compared with these 2 figures, it is shown that a sodium titanate ($Na_2Ti_5O_{11}$) hydrogel was created in both samples. However, titanium oxides (anatase and rutile) were found in 5M-W-H specimen, which was introduced from the reaction between oxygen and Ti-6Al-4V substrate during heat treatment in atmospheric condition. Due to relatively lack of oxygen in the vacuum condition, the titanate phase could not be noticed in the 5M-W-V sample. Nevertheless, a series of clear HA peaks were arisen in the XRD patterns after soaking in m-SBF for 5 days on both specimen, and the strength of HA peaks was increased with soaking period of time in m-SBF.

The results evidently show that the bioinert Ti-6Al-4V has been successfully bioactivated via alkali-DI water- heat treated techniques. A layer of bone-like apatite was successfully generated along the sample surfaces after immersing in m-SBF for 5 days. Interfacial mechanical bonding test will be carried out for the treated specimen in the future to confirm such beneficial effects.

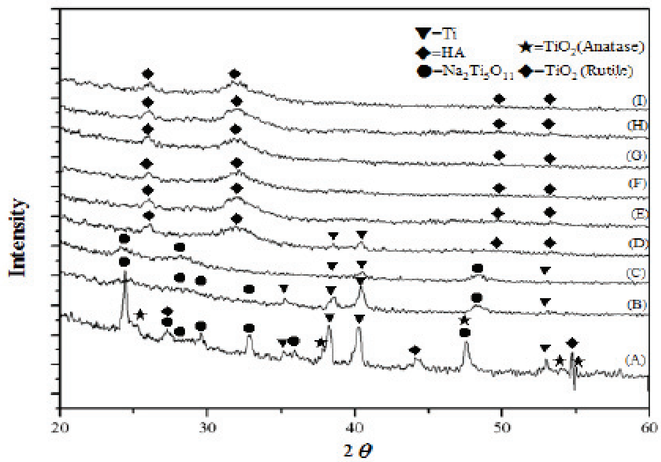

Fig. 5. XRD patterns of 5M-W-H set samples in m-SBF for various days: (a) 0; (b) 1; (c) 3; (d) 5; (e) 7; (f) 14; (g) 17; (h) 21; (i) 28 days, respectively.

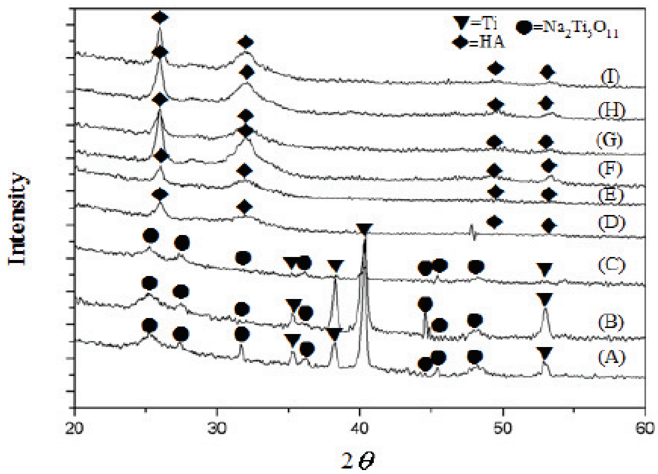

Fig. 6. XRD patterns of 5M-W-V set samples in m-SBF for various days: (a) 0; (b) 1; (c) 3; (d) 5; (e) 7; (f) 14; (g) 17; (h) 21; (i) 28 days, respectively.

4. Conclusions

The 5M-W-H sample has the relatively thicker bioactive sodium titanate hydrogel, which also contains rich titanate phases in the coating structure. The 5M-W-H has the lowest contact angle value among entire specimens, which is expected to have favourable bone-like apatite inducement ability. A layer of bone-like apatite was successfully generated along the alkali-DI water- heat treated sample surfaces after immersing in m-SBF for 5 days.

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